(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
8 July 2004 (08.07.2004)

PCT

(10) International Publication Number
WO 2004/056204 A1

(51) International Patent Classification[7]: A23L 1/30, 1/05, C12P 19/04

(21) International Application Number: PCT/EP2003/012602

(22) International Filing Date: 11 November 2003 (11.11.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
02080467.0 19 December 2002 (19.12.2002) EP

(71) Applicant *(for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GA, GE, GN, GQ, GW, HR, HU, ID, IS, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MD, MG, MK, ML, MR, MX, MZ, NE, NI, NO, PH, PL, PT, RO, RU, SE, SK, SN, SY, TD, TG, TJ, TM, TN, TR, UA, UZ, VN, YU only)*: **UNILEVER N.V.** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant *(for AE, AG, AU, BB, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, OM, PG, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only)*: **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London, Greater London EC4P 4BQ (GB).

(71) Applicant *(for IN only)*: **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, 400 020 Mumbai (IN).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **BRUGGEMAN, Yvonne, Evelien** [NL/NL]; Unilever R & D Vlaardingen, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL). **RAVESTEIN, Peter** [NL/NL]; Unilever R & D Vlaardingen, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL).

(74) Agent: **VAN VELZEN, Maaike**; Unilever Patent Department, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: POLYMER COMPOSITION SUITABLE FOR USE IN FOOD PRODUCTS

(57) Abstract: Polymer compositions comprising a glyceride and least 1 building block covalently linked via phenolic residues preferably containing an ortho methoxygroup, wherein the building blocks are selected from the group of proteins (P), glycerides (G) and polysaccharides (S) and wherein the covalent linkage is between P-G, G-G, G-S or combinations thereof show good emulsifying, thickening and stabilising properties. The polymers are suitable for use in food products, especially emulsions and foams.

WO 2004/056204 A1

Polymer composition suitable for use in food products

Field of the invention

The current invention relates to a polymer composition comprising a glyceride and a building block covalently linked via phenolic residues.

Background of the invention

Biopolymers are extensively used in food products as emulsifiers, gelling agent, structuring agents, stabilisers, thickeners and the like. Especially biopolymers such as starches, protein and triglycerides are well known and are used for example in sauces, margarine, dressings, soups and many other food compositions.
Many of the polymers are naturally occurring and show good functionality in relation to the above mentioned features.

However there is still a need for alternative compositions with improved functionality and controlled characteristics. This desire is exemplified in WO-A-96/03440, which discloses a method for gelling or increase of viscosity of aqueous media containing gellable polymeric materials having substituents with phenolic hydroxyl groups. This document specifically discloses the gelation of arabinoxylans or pectins by adding an effective amount of a laccase to an aqueous medium containing these substituents. Furthermore it is disclosed that proteins having one or more tyrosine residues in the amino acid sequence can be gelled by use of a laccase. The resulting compounds are indicated as thickening and/or stabilising agents.

The compositions disclosed in WO-A-96/03440 rely on the gelation of single compositions and hence lead to gels with a limited variety in composition and functionality.

It is therefore an object of the current invention to provide polymers which can be used in a variety of food products and which enlarge the group of currently available polymers for use in foods. The invention especially relates to polymers suitable for stabilising oil and water containing emulsions and foams.

Summary of the invention

It has surprisingly been found that specific polymers of a glyceride and a molecule (M) selected from the group of protein, polysaccharides and/or glycerides meet the above objective. Especially those polymers consisting of a polysaccharide and a fatty acid glyceride unit were found to be good emulsifiers and/or stabilisers.

Therefore the invention relates to a polymer composition comprising a glyceride and a molecule (M) selected from the group comprising proteins (P), glycerides (G) and polysaccharides (S), wherein the molecule (M) and the glyceride are covalently linked via phenolic residues forming polymer building blocks of P-G, G-G, G-S or combinations thereof.

The invention further relates to food products containing these polymers and to a method for preparation of these polymers.

Detailed description of the invention

The polymers according to the invention are composed of glycerides and molecules (M) which together form building blocks. Building blocks are polymer units which comprise a glyceride and a molecule (M) selected from the group comprising glycerides, proteins and polysaccharides. The glyceride and molecule (M) are covalently linked by 2 connected phenolic residues. This covalent bond is an essential part of the claimed polymers. The individual building blocks may be linked together via further covalent bonds, preferably between 2 phenolic residues.

The building blocks of the polymers according to the invention comprise glycerides and at least one of polysaccharides (S), glycerides (G) and proteins (P).

Glycerides in the context of the invention are glycerol based molecules wherein the glycerol backbone is covalently linked to at least one residue such as a fatty acid, or another hydrophobic acid, aldehyde or ketone e.g. retinoic acid, phenolics, sterols, tocopherols. Well known glycerides are mono, di and tri acyl fatty acid glycerides. Mono- and diglycerides are already known for their emulsifying capacity. Triglycerides are well known texturing agents in products such as margarine, butter, creams.

The glycerides may contain any fatty acid, both naturally occurring and synthetic ones.

Preferred fatty acids have a chain length of from 10 to 24 carbon atoms, more preferred from 16 to 20 carbon atoms. Suitable fatty acids include oleic acid, stearic acid, palmitic acid linoleic and linolenic acid.

Most preferred, the glyceride in the building block is a diglyceride.

Molecule (M) optionally is a protein. Proteins are chains of covalently linked amino acids whereby it is possible to use any desired protein. Preferred proteins contain at least one lysine amino acid residue. Food grade proteins are preferred and hence protein is preferably selected from the group of dairy proteins such as casein and whey protein, vegetable proteins, especially soy protein and egg protein or gelatin.

The third potential molecule of a building block is polysaccharide. Any polysaccharide can be used in the polymers according to the invention but preferred are those polysaccharides which in their naturally occurring form contain a phenolic residue such as ferulic acid, vannilic acid, coumaric or cinnamic acid esterified to (M). Sugar beet pectin and arabinoxylanes isolated from cereals are examples of polymers that contain ferulic acid residues in their naturally occurring form. These compositions are described in more detail by Lex Oosterveld , Carbohydrate research 300, 179-181, 1997 and thesis Lex Oosterveld, Landbouwuniversiteit Wageningen Netherlands, 16.12.1997, ISBN 90-5485785-4.

The glyceride and molecule (M) in the polymer comprise a link via two phenolic residues. This link is a covalent bond. It is preferred that the phenolic residue that is participating in the covalent bond comprises a radical stabilising group in ortho position in the phenolic ring. The substituent is preferably such that the resulting compound is food grade. An example of a very suitable electron-withdrawing group is the methoxygroup, positioned ortho with respect to the hydroxyl group.

Examples of covalent bonds between two phenolic residues are described by Oosterveld (thesis Lex Oosterveld 1997) and in US 5,786,470. Preferably the phenolic residue is derived from the group of vanillic acid, ferulic acid, coniferol, caffeic acid, chlorogenic acid.

Figure 1 is one example of a specific covalent bond between the two phenolic residues. Other forms of covalent bonding are also encompassed within the invention.

The polymer according to the invention comprises a glyceride and at least another molecule selected from protein, glyceride, polysaccharide or a combination thereof. Embodiments wherein n building blocks are linked to obtain a large linear polymer are also encompassed within the invention. Further encompassed in the invention are polymers wherein building blocks are linked via at least 2 phenolic residues or by other (non) covalent linkages. The polymers according to the invention may be both linear and branched polymers.

In the polymers the covalent linkage is between P-G, G-G, G-S, or combinations thereof.

These alternative embodiments are described below.

In a first embodiment, the polymer comprises covalently linked proteins and glycerides, preferably diglycerides. These polymers when branched form fat-protein networks which may be applied as structuring agents.

In another embodiment the polymer comprises covalently linked polysaccharides and glycerides, preferably diglycerides. An example of such a composition is shown in figure 1. These compositions were found to be suitable emulsifiers which may be used to stabilise oil and water containing compositions. In

such compositions the polymers are found at the oil/water interface whereby the fatty acid chains are in the oil phase and the polysaccharide part is in the aqueous phase. Preferred glycerides for this purpose are diglycerides containing fatty acids derived from sunflower oil, soybean oil, rapeseed oil, maizgerm oil, olive oil, line oil, peanuts, cottonseed oil, and safflower oil, butter fat.
Preferred polysaccharides for this purpose are selected from the group comprising pectins from sugar beet, arabinoxylanes, starches. These polysaccharides may naturally comprise a phenolic group or may have been functionalised with such group.

According to a further embodiment the polymer comprises covalently linked glycerides. The glycerides may be mono or diglycerides with any suitable fatty acid. These polymers preferably contain a multiplicity (n) of glyceride building blocks, with a preference for n between 2 and 1000.
Such polymers may be used to structure a fat phase for example in a margarine type food composition.

Preferred polymers are those wherein a glyceride is covalently linked to a polysaccharide or protein. Most preferred compositions are those wherein a glyceride is covalently linked to a polysaccharide because these polymers were found to have emulsion stabilising properties.

The polymers according to the invention comprise at least 2 phenolic ring systems. Surprisingly these were found to enhance the stability of unsaturated fatty acid residues that may be part of the polymer and of other oxidation sensitive compositions in the same product. Without wishing to be bound by any theory, applicants believe this is due to the mesomeric

ring system which can trap radicals which would otherwise cause oxidation of the double carbon-carbon bond.

As indicated above, the polymers according to the invention may suitably be applied in food products, whereby depending on their composition the properties of the food product may be influenced. Their use is especially recommended in oil and water containing compositions.
Therefore in a further aspect the invention relates to food products containing said polymers.

The following beneficial characteristics of these compositions have been identified.
$(G\text{-}G)_n$ which are referred to as acyl-glycerol-phenolic acid hybrids, have superior emulsifying properties especially in oil and water containing compositions of relatively low fat content (i.e. between 10 and 60 wt% fat). Furthermore these compositions may be used as texturising agents, imparting viscosity and/or structure to a composition.

Furthermore these compositions, especially (G-G)n (n equal to or higher than 1) containing polymers are suitable for encapsulation of ingredients such as flavour compounds or functional ingredients. To make such (G-G)n compositions, it is preferred to start from monoglycerides functionalised with two phenolic acid groups.

Polymers containing (G-S)n wherein n is preferably 1, were found to stabilise oil and water containing compositions. Furthermore these compositions when included in a two phase system such as water and oil, can fix particles or micro-organisms in one of the phases.

Therefore in a further aspect, the invention relates to an oil and water containing emulsion, preferably an oil in water emulsion, comprising a polymer according to invention.

In a preferred embodiment, the invention relates to an oil and water emulsion comprising from 20 to 80 wt% fat and from 0.1 to 10 wt% of said polymer. Even more preferred, the polymer comprises covalently linked glyceride and polysaccharide.

The polymers according to the invention are prepared from glycerides and molecule (M) under suitable circumstances to form a covalent bond. In a further aspect the invention relates to a method for the preparation of said polymer, wherein a composition comprising the elements of the building blocks is treated with an oxidative enzyme. This treatment may suitably be carried out in presence or absence of a solvent. For most cases, the use of an aqueous medium is preferred. However for example in case of the preparation of a glyceride-glyceride hybride polymer, no solvent is needed as long as the oxidation enzyme is functional. The latter can for example be obtained by using well known immobilisation methods for the enzyme.

Before oxidation takes place the molecules (building block elements) that form the starting composition in this reaction are preferably functionalised with one or more phenolic residues, preferably containing an ortho methyxygroup with respect to the hydroxyl group. It will be appreciated that functionalisation is not needed for molecules that naturally contain phenolic residues.
Said functionalisation may be obtained through natural occurrence of said phenolic groups in the element of a building

block or by synthetic functionalisation of said phenolic groups to the respective molecule. It will be appreciated that naturally occurring polymers with phenolic groups are preferred.

In the oxidation reaction the phenolic groups are covalently linked. An example of a possible covalent link is shown in figure 1.

The oxidation may be carried out in any way known in the art . Both enzymatic oxidation and chemical oxidation routes may be used. Enzymatic oxidation is preferred. Suitable enzymes that can catalyse the formation of the covalent bond are peroxidase, laccase, polyphenol oxydases. Peroxidase is the preferred enzyme.

In case an enzymatic oxidising system is applied, the enzyme is preferably added in the form of a solution or a dispersion in an aqueous buffer system.

Some enzymes, such as peroxidases, require the presence of a co-oxidant such as hydrogen peroxide for their activity. The co-oxidant is preferably added separately from the enzyme that requires it's presence.

The amount of enzyme added is expressed in terms of activity units. Preferably enzyme is present in excess.

If the oxidation is carried out enzymatically, the temperature during oxidation is preferably from 20 to 60 °C. Most preferred the temperature is around the temperature at which the enzyme shows maximum activity.

In case a chemical oxidant is applied, the oxidant is preferably added in the form of a diluted aqueous solution.

The introduction of a phenolic residue is described below for each of the potential elements of building blocks.

Polysaccharides

Well known esterification conditions may be used for introduction of a phenolic group on the polysaccharide chain.

Protein

Some proteins naturally contain amino acids with phenolic residues. The preparation of a protein containing phenolic residues is straightforward. Any possible covalent link e.g. via esterification is suitable.

Glycerides

Di/mono -glycerides containing at least one phenolic residue are preferably prepared by interesterification of a triglyceride oil with the ester form of the phenolic residue. Examples of the latter are ferulic acid ester with para position esterified to an alcohol, vanillic acid ester with para position esterified to an alcohol or caffeic acid ester with para position esterified to an alcohol.
Said interesterification reaction can be carried out with chemical or enzymatic catalysts. The use of lipase as catalyst is preferred.

In a preferred embodiment the invention relates to a method wherein a polymer comprising covalently linked diacylglyceride and polysaccharide is prepared, comprising the steps of
a) preparing a feruloyl diglyceride by transesterification of

triacylglycerol with a phenolic compound containing a methoxygroup in ortho position with respect to the hydroxyl group;

b) providing a polysaccharide composition containing a phenolic hydroxygroup containing a methoxygroup in ortho position;

c) subjecting the composition according to (a) and (b) to treatment with an oxidative enzyme.

It will be appreciated that the exact reaction conditions in terms of temperature, ratio between the elements of the building blocks and type/amount of catalyst/enzyme, determine the final product composition in terms of polymer length and composition.

The invention is illustrated by the following examples.

Examples

Example 1

Synthesis of feruloylated diglyceride (DG-F)

DG-F was synthesised following the method disclosed by Compton (JAOCS, vol 77, no 5, 2000, pages 513-519)preparing feruloyl diolein starting from triolein.

The synthesis was performed without the use of solvent. Ethylferulate (3.58 g) was dissloved in 40 g triolein at 60°C. Novozyme 435 (3.55 g) (a lipase) was added and the reaction was allowed to proceed for 7 days at 60°C under continuous mixing.

Purification

5.3 g of the reaction mixture was brought onto a Silicagel 60 (Merck) column (3.5 cm diam., 25 cm height). The mixture was subsequently separated by elution with solvent mixes with increasing polarity in the following order: petroleum ether : diethyl ether = 4:1 (v/v), petroleum ether : diethyl ether = 7:3 (v/v), petroleum ether : diethyl ether = 3:2 (v/v) and finally by elution with diethyl ether. Fractions of approximately 200ml were collected, solvent was removed by evaporation and analysis was done by means of thin layer chromatography on Kieselgel 60 F254 plates (Merck) using a mixture of toluene: diethyl ether = 4:1 (v/v).

Emulsion tests for controls

11.85 g sunflower oil, 3 ml water and 0.15g of either Admul Wol^{tm}, (comparative example) total transesterification mix (comparative example) or purified DG-F (comparative example) were mixed and emulsified by vigorous stirring for approximately one minute.

No emulsifying properties were observed for purified DG-F or the total transesterification mix. The phases started to separate within two hours standing at room temperature.

Crosslinked polymer according to the invention

In situ preparation of emulsifier: crosslinking of DG-F and pectin-F with laccase to yield DG-F-F-pectin.

A number of test tubes were filled as given in the table. The conditions of each experiment are outlined in table 1. Tube 1-7 and Tube 10-12 are control experiments, which are not according to the invention. Tubes 8,9 are according to the invention.

All tubes were prepared at room temperature.

First the tubes were stirred vigorously on a Vortex mixer for 30 seconds.

Next the enzyme was added (or not) and mixing was done for another 30 seconds.

Tubes were left at RT and photographed.

Table 1

Tube number	Gram Sunflower oil	mg DG-F	µL water	µL 5 % pectin	µL 1% pectin	Laccase
1	1.69	-	429	-	-	yes
2	1.69	-	286	143	-	yes
3	1.69	-	286	-	143	yes
4	1.69	-	429	-	-	no
5	1.69	-	286	143	-	no
6	1.69	-	286	-	143	no
7	1.69	21.4	429	-	-	yes
8	1.69	21.4	286	143	-	yes
9	1.69	21.4	286	-	143	yes
10	1.69	21.4	429	-	-	no
11	1.69	21.4	286	143	-	no
12	1.69	21.4	286	-	-	no

Pectin = Kelco pectin in water (w/v)
Enzyme = Novo Lacase PPL, SP710, PX 5326, 10 µL of a 1:10 dilution in water was added.

Stable emulsions without phase separation of the oil and water phase were only obtained when DG-F and pectin was present and a crosslinking enzyme was used. This confirms that the polymer comprising diglyceride linked to pectin via a ferulic acid-ferulic acid covalent bond is a good emulsifier for oil/water systems.

Claims

1. Polymer composition comprising a glyceride and a molecule (M) selected from the group comprising proteins (P), glycerides (G) and polysaccharides (S), characterised in that the molecule (M) and the glyceride are covalently linked via phenolic residues forming polymer building blocks of P-G, G-G, G-S or combinations thereof.

2. Polymer composition according to claim 1 wherein a glyceride is covalently linked to a polysaccharide or a protein.

3. Polymer composition according to claim 1 or 2 wherein the glyceride is a diglyceride.

4. Polymer composition according to any of claims 1-3 wherein the phenolic residue is selected from the group of vanillic acid, ferulic acid, caffeic acid, coniferol, chlorogenic acid.

5. Polymer composition according to any of claims 1-4 wherein the polymer comprises a diglyceride covalently linked to a polysaccharide.

6. Food product comprising a polymer composition according to any of claims 1-5.

7. Oil and water containing emulsion comprising a polymer according to any of claims 1-5.

8. Oil and water emulsion comprising from 20 to 80 wt% fat and from 0.1 to 10 wt% of a polymer according to any of claims

1-5.

9. Oil in water emulsion according to claim 7 or 8 wherein the polymer comprises covalently linked glyceride and polysaccharide.

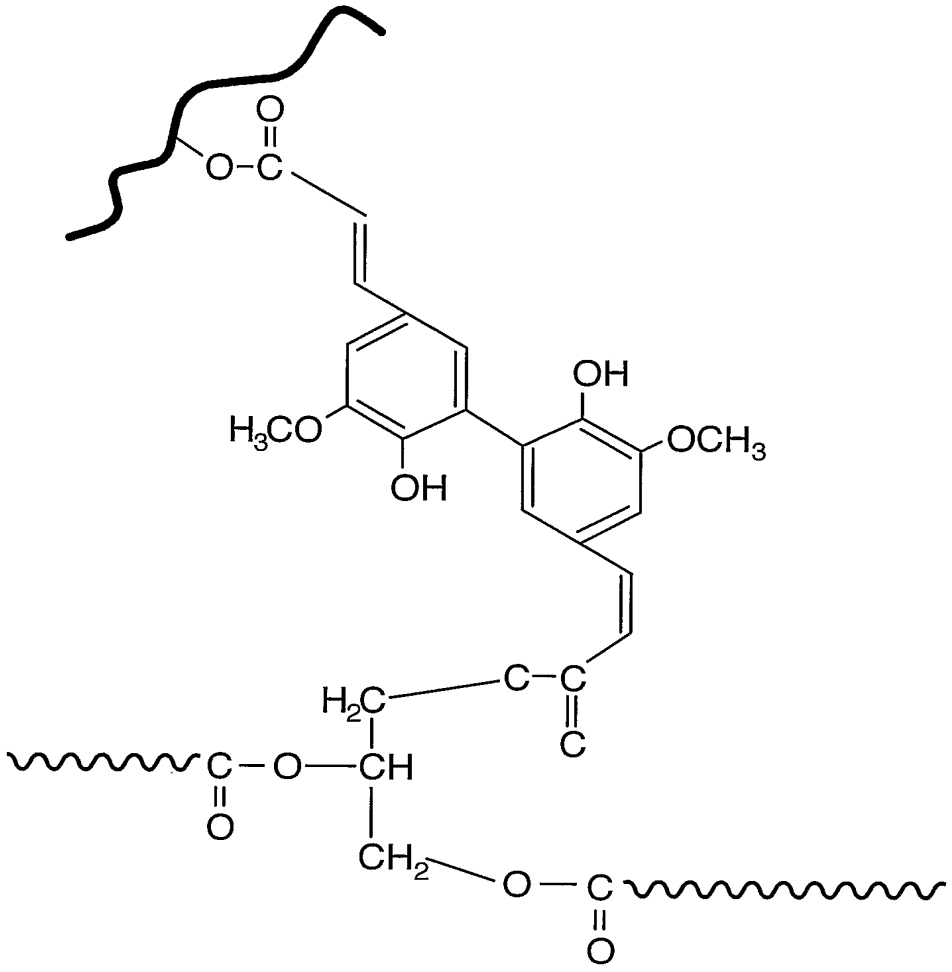
10. Method for the preparation of a polymer according to claim 1, wherein a composition comprising the glyceride and molecule (M) is treated with an oxidative enzyme.

11. Method according to claim 10 wherein a polymer comprising covalently linked diacylglyceride and polysaccharide is prepared, comprising the steps of
a) preparing a feruloyl diglyceride by transesterification of triacylglycerol with a phenolic compound containing a methoxygroup in ortho position with respect to the hydroxyl group;
b) providing a polysaccharide composition containing a phenolic hydroxygroup containing a methoxygroup in ortho position with respect to the hydroxyl group;
c) subjecting the composition according to (a) and (b) to treatment with an oxidative enzyme.

12. Use of a polymer according to claim 1 for the encapsulation of ingredients.

13. Use according to claim 12 wherein the polymer is a polyglyceride (G-G)n.

Fig.1.



= Carbohydrate backbone

= Fatty acid

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/12602

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A23L1/30 A23L1/05 C12P19/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A23L C12P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, COMPENDEX, PAJ, WPI Data, BIOSIS, MEDLINE, FSTA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96/03440 A (NOVONORDISK AS ;BUDOLFSEN GITTE (DK); HELDT HANSEN HANS PETER (DK)) 8 February 1996 (1996-02-08) cited in the application the whole document	1-13
A	DATABASE COMPENDEX 'Online! ENGINEERING INFORMATION, INC., NEW YORK, NY, US; COMPTON DAVID L ET AL: "Lipase-catalyzed synthesis of ferulate esters" XP002234471 Database accession no. E2000295196342 cited in the application abstract	1-13

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 March 2004	12/03/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Vernier, F

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	& JAOCS J AM OIL CHEM SOC;JAOCS, JOURNAL OF THE AMERICAN OIL CHEMISTS' SOCIETY 2000 AMERICAN OIL CHEMISTS' SOC, CHAMPAIGN, IL, USA, vol. 77, no. 5, 2000, pages 513-519,	
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 056 (C-566), 8 February 1989 (1989-02-08) & JP 63 246350 A (YAMASA SHOYU CO LTD), 13 October 1988 (1988-10-13) abstract	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 03/12602

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9603440 A	08-02-1996	AT 198604 T	15-01-2001
		AU 3074595 A	22-02-1996
		BR 9508350 A	04-11-1997
		CA 2195640 A1	08-02-1996
		CZ 9700205 A3	14-05-1997
		DE 69519852 D1	15-02-2001
		DE 69519852 T2	02-08-2001
		WO 9603440 A1	08-02-1996
		EP 0750641 A1	02-01-1997
		ES 2155523 T3	16-05-2001
		FI 970274 A	23-01-1997
		HU 77999 A2	28-04-1999
		JP 10502962 T	17-03-1998
		PT 750641 T	29-06-2001
		US 6232101 B1	15-05-2001
JP 63246350 A	13-10-1988	NONE	

DERWENT-ACC-NO: 2004-533719

DERWENT-WEEK: 200474

TITLE: Polymer composition useful as emulsifier and stabilizer in food products comprises glyceride and building block covalently linked via phenolic residue

INVENTOR: BRUGGEMAN Y E; RAVESTEIN P

PATENT-ASSIGNEE: HINDUSTAN LEVER LTD[UNIL] , UNILEVER NV[UNIL] , UNILEVER PLC[UNIL]

PRIORITY-DATA: 2002EP-080467 (December 19, 2002)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE
WO 2004056204 A1	July 8, 2004	EN
AU 2003289862 A1	July 14, 2004	EN

DESIGNATED-STATES: AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH CN CO CR CU CZ DE DK DM DZ EC EE EG ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NI NO NZ OM PG PH PL PT RO R U SC SD SE SG SK SL SY TJ TM TN TR TT TZ UA UG US UZ VC VN YU ZA ZM ZW AT BE BG BW CH CY CZ DE DK EA EE ES FI FR GB GH GM GR HU IE IT KE LS LU MC MW MZ NL OA PT RO SD SE SI SK SL SZ TR TZ UG ZM ZW

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
WO2004056204A1	N/A	2003WO-EP12602	November 11, 2003
AU2003289862A1	Based on	2003AU-289862	November 11, 2003

INT-CL-CURRENT:

TYPE	IPC DATE
CIPS	A23L1/00 20060101
CIPS	A23L1/03 20060101
CIPS	A23L1/035 20060101
CIPS	A23L1/0524 20060101
CIPS	A23L1/09 20060101
CIPS	C12P21/00 20060101
CIPS	C12P7/64 20060101

ABSTRACTED-PUB-NO: WO 2004056204 A1

BASIC-ABSTRACT:

NOVELTY - Polymer composition (C1) comprises a glyceride and a molecule (M) selected from proteins (P), glycerides (G) and polysaccharides (S). (M) And the glyceride are covalently linked via phenolic residues forming polymer building blocks of P-G, G-G and/or G-S.

DESCRIPTION - INDEPENDENT CLAIMS are included for

(1) preparation of a polymer (R1) involving treatment of (C1) with an oxidative enzyme; and

(2) oil and water containing emulsion comprising (R1).

USE - In food products (claimed) as an emulsifier, gelling agent, structuring agent, stabilizers, thickeners; for the encapsulation of ingredients e.g. flavor compounds; for stabilizing oil and water containing emulsions and foams and as a thickening agent.

ADVANTAGE - The polymers exhibit improved stabilizing and/or emulsifying properties for oil and water containing emulsions and foams.

EQUIVALENT-ABSTRACTS:

POLYMERS

Preferred Process: Preparation of (R1) comprising covalently linked diacylglyceride and polysaccharide involves:

(a) preparing a feruloyl diglyceride by transesterification of triacylglycerol with a phenolic compound containing a methoxy group in ortho position with respect to hydroxyl group; and

(b) treating the mixture of a feruloyl diglyceride and a polysaccharide composition comprising a phenolic hydroxy group containing a methoxy group in ortho position with respect to the hydroxyl group, with an oxidative enzyme.

Preferred Components: A glyceride (preferably diglyceride) is covalently linked to (S) or (P). The phenolic residue is vanillic acid, ferulic acid, caffeic acid, coniferol or chlorogenic acid. (R1) Comprises a diglyceride covalently linked to (S1). The emulsion comprises (wt.%): fat (20 - 80) and (R1) (0.1 - 10). (R1) Is a polyglyceride (G-G)n.

n = at least1.

Ethylferulate (3.58 g) was dissolved in triolein (40 g) at 60degreesC. Novozyme 435 (RTM; alipase) (3.55 g) was added and the reaction was allowed to proceed for 7 days at 60degreesC under stirring. The reaction mixture (5.3 g) was purified on silica gel column to obtain purified feruloylated diglyceride (DG-F). The in-situ preparation of emulsifier was carried out by coupling of DG-F and protein-F to yield DG-F-F-protein in the presence of enzyme. The test tube were filled with following components: sunflower oil (1.69 g), DG-F (21.4 mg), water (286 ml), kelco pectin in water (5 wt./vol.%) (143 mul), and Novo Lacase PPL (RTM; enzyme) (10 mul of 1:10 dilution in water) at room temperature and a control samples were prepared without adding an enzyme or pectin. Test tubes were stirred vigorously on a vortex mixer for 30 seconds before addition of enzyme (or not) and mixing was done for another 30 seconds. The tubes were left at room temperature and it was found that stable emulsion without phase separation of oil and water was only obtained when DG-F and pectin was present and an enzyme was used. This indicated that the polymer comprising diglyceride linked to pectin via a ferulic acid-ferulic acid covalent bond was a good emulsifier for oil/water system.

TITLE-TERMS: POLYMER COMPOSITION USEFUL EMULSION STABILISED FOOD PRODUCT COMPRISE GLYCERIDE BUILD BLOCK COVALENT LINK PHENOLIC RESIDUE

DERWENT-CLASS: A11 A97 D13

CPI-CODES: A10-E07; A12-W09; A12-W12C; D03-H01J; D03-H01N;

ENHANCED-POLYMER-INDEXING: Polymer Index [1.1] 2004 ; G3623*R P0599 D01 G3714*R F70; L9999 L2391; L9999 L2186*R; L9999 L2813; M9999 M2186; M9999 M2813;

Polymer Index [1.2] 2004 ; ND01; Q9999 Q9110; Q9999 Q7589*R; Q9999 Q9347; Q9999 Q7523; ND03;

Polymer Index [1.3] 2004 ; C999 C044 C000; C999 C271;

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: 2004-196243